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Report 2330

DETERMINATION OF LOW-LEVEL CONCENTRATIONS OF LEAD IN PAINT

by
Dario A. Emeric

July 1981

U.S. ARMY MOBILITY EQUIPMENT
RESEARCH AND DEVELOPMENT COMMAND
FORT BELVOIR, VIRGINIA

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19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

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20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

Report describes an instrumental method of analysis to provide a direct-reading emission spectroscopic technique to the problem of analyzing oil-base paints for low-level concentrations of lead or any other element of interest.

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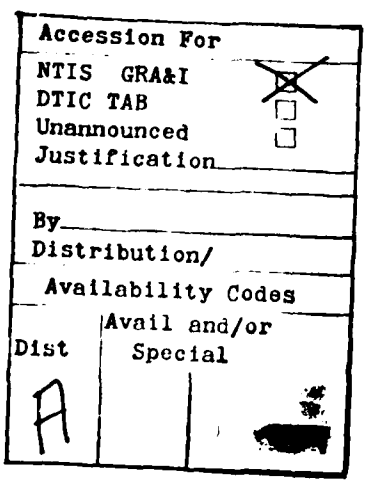

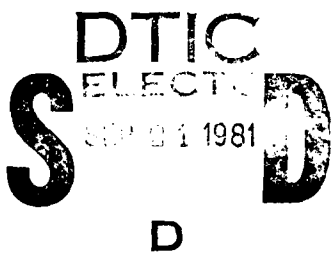

DETERMINATION OF LOW-LEVEL CONCENTRATIONS OF LEAD IN PAINTS

I. INTRODUCTION

1. **Statement of the Problem.** This investigation was undertaken to provide a direct-reading emission spectroscopy technique to the problem of analyzing oil-base paints for low-level concentrations of lead or any other element of interest.

2. **Background.** Public Law 94-317 (Lead-Based Paint Poison Protection Act of 1976) limits lead to a maximum content of 0.06 percent (600 p/m) by weight in certain paints and tinting colors. Atomic absorption spectroscopy is the only accepted procedure of the American Society Testing of Materials (ASTM) for analysis of lead in paints. (See ASTM Method D-3335 Low Concentrations of Lead in Paint by Atomic Absorption Spectroscopy.) This procedure is time consuming, requiring extensive handling of the sample to reduce it to a form suitable for the determination of lead. Military Specification MIL-E-52798, "Enamel, Alkyd, Camouflage," has an alternate method using X-ray fluorescence on a dried film. Other methods for analysis of lead in liquid paint are: anodic stripping voltammetry by Environmental Sciences Associates for acrylic and latex paints, and X-ray fluorescence by Princeton Gamma Techniques.

An emission spectroscopic technique has been developed which will provide a rapid analytical method to analyze for lead in liquid oil-base paints. This procedure may also be used for the quantitative determination of other elements of interest (such as chromium) in liquid oil-base paints. A drastic savings in time and manpower could be achieved by using this direct-reading emission spectrometric technique for the analysis of paints for their lead content. This technique makes use of the rotating disk electrode system, specifically designed for the analysis of liquid samples. The samples and the standards are excited in an electric arc or spark discharge. The light intensity will vary directly with the lead content of the samples and the standards. The lead content of the unknown samples may be found by comparing their intensity values with the plotted intensity values of the standards.

II. EXPERIMENTAL PROCEDURE

3. **Approach to the Problem.** Laboratory experiments were carried out to investigate variables as: shelf life of the paint standard (prepared in-house), consequences of delays in the analysis of the samples, analytical parameters (source type, preburn time, exposure time, circuit capacitance and inductance), precision, sensi-

tivity, sample preparation, etc. Paint formulations of MIL-E-52798 and TT-P-636 ("Primer, Coating, Alkyd, Wood and Ferrous Metal") were prepared with lead contents ranging from blank to 0.055 percent based on total paint or from blank to 0.09 percent based on nonvolatile vehicles. In addition, paint formulations of MIL-P-52977 ("Red Oxide Primer Lead- and Chromium-free Paint") were also prepared. The lead and chromium contents of all of these standards were verified by atomic absorption spectroscopy according to ASTM Method D-3335. Commercial samples that conformed to the above-mentioned specifications were obtained and were analyzed by atomic absorption spectroscopy and by emission spectroscopy (the subject method). The standards, in storage, were checked on a periodic basis by atomic absorption and the subject emission spectroscopic method of analyses to determine their shelf life.

III. RESULTS

4. **Laboratory**. The analytical parameters of the 0.75-m Jarrell-Ash Model 750 Atom Counter Spectrometer selected for the analysis of the paints are as follows:

Wavelength: 283.3 nanometers – lead.
Wavelength: 267.7 nanometers – chromium.
Flushing gas: carbon dioxide ($C0_2$).
Mode of excitation: high-voltage spark.
Capacitance: residual.
Inductance: 31- microhenries.
Resistance: residual.
Repetition rate: 4 breaks/½ cycle.
Current: 4 amperes.
Gas flow rate: 25 standard cubic feet per hour.
Preflush: 5 seconds.
Preburn: 6 seconds.
Exposure: 20 seconds.
Background: 442.4 nanometers (hydrogen).
Counter electrode: ASTM C-5.
Rotating disk: ASTM D-1.

The paint samples could not be analyzed as received because the paint spattered and coagulated on the rotating disk. The samples and standards were diluted 1:1 with nondrying oils such as alkali-refined linseed oil and soybean oil to overcome the problem of spattering and coagulation. Although linseed oil could be used as well as soybean oil, we selected the latter because it is nontoxic and has a higher autoignition temperature.

It was noted that paint samples were polymerizing (forming skins) during early storage. To avoid loss of analyzable lead in the standards, they were diluted 1:1 with clarified raw soybean oil. This dilution accomplished several purposes: (a) It protected the paint from oxidation or drying, (b) it provided standard samples having the same dilution at all times, and (c) it provided good storage stability. The stored standards (diluted with soybean oil) were reanalyzed by ASTM Method D-3335 after 2 and 9 months; no changes were observed in the lead content. The lead content was also reanalyzed by emission spectroscopy, and in 11 months, the lead content was found to be virtually unchanged. The results obtained by atomic absorption and by emission spectroscopy are shown in the table.

	Atomic Absorption (%)		Atomic Emission (%)	
Sample	Chromium	Lead	Chromium	Lead
TB145		0.004		0.005
TB146		0.003		0.005
TB153		0.002		0.005
TB172		0.005		0.006
TB178	0.085*	0.008	0.08*	0.009
0.015%Pb		0.014		0.014
0.055%Pb		0.056		0.053

* Simultaneous analysis with lead. Although the objective of this investigation concerned lead, it was broadened slightly to incorporate chromium, in a limited fashion.

Results are in percent based on total paint. Different paint standards, their lead and/or chromium content already verified by atomic absorption have been used as unknowns in order to check the spectroscopic results.

IV. DISCUSSION.

5. **Discussion.** Although experimental data obtained during the course of this investigation has indicated the feasibility of utilizing an emission spectroscopic technique for the determination of low levels of lead in liquid oil-base paints, a number of precuations must be observed. Since this procedure utilizes a noncompensated rotating-disk-method excitation stand, it is sensitive to the viscosity of the various specification paints and, therefore, individual standard working curves must be prepared for each of the paint specifications. Also, paint standards (known lead content) always should be carried along when an unknown product is being analyzed. This method should be considered applicable to oil-base paints only and, even then, should

be checked for compatibility when other oil-base paint specifications are used. Finally, fast-drying oil-base paints may be incompatible with this procedure as they may tend to coagulate on the rotating disk and spatter in spite of the 1:1 dilution with a non-drying oil.

V. CONCLUSIONS

6. Conclusions. It is concluded that:

a. A rapid and convenient emission spectroscopic technique has been developed for the quantitative determination of lead in liquid oil-base paints.

b. This technique may be utilized as an alternate to an atomic absorption spectroscopic method for the determination of lead (ASTM D-3335).

c. This technique may be applied to the analyses of other elements of interest in liquid oil-base paints.

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Environmental Sciences Associates Inc., "The Direct Analysis of Lead in Liquid Paint by Anodic Stripping Voltammetry."

Federal Specification TT-P-636, "Primer, Coating, Alkyd, Wood and Ferrous Metals."

Military Specification MIL-E-52798, "Enamel, Alkyd, Camouflage."

Military Specification MIL-P-52977, "Red Oxide Primer."

Princeton Gamma-Tech-PGT Model 100 Chemical Analyzer for Lead in Paint Analysis.

APPENDIX

ANALYTICAL PROCEDURE FOR DETERMINING LEAD IN OIL-BASE PAINTS

1. **Equipment and Materials.**

   a. **Apparatus:**

   (1) Direct-reading emission spectrometer with rotating disk capabilities.

   (2) Graphite disk electrode – ASTM D-1.

   (3) Graphite counterelectrode – ASTM C-5.

   (4) Sample holder that will fit the spectrometer (plastic cap or boat).

   (5) Disposable graduated pipettes and cups.

   (6) One-half-pint paint cans.

   b. **Reagents:** Clarified soybean oil.

2. **Procedure.**

The standard paints ranging in concentration from blank to 0.06 percent (based on total paint) are shaken or stirred to assure uniformity. A portion of each standard concentration is analyzed by atomic absorption spectroscopy (ASTM D-3335) or any other acceptable standard method. The remainders of each of the standard samples are diluted 1:1 with soybean oil in an appropriate-sized can and shaken or stirred until uniform. The paint standards containing the soybean oil as well as the unknown (diluted 1:1 with soybean oil) are poured into a suitably sized bottle cap or a boat and analyzed using the parameters described in the list (page 2). Prepare calibration curves, if necessary, by plotting counts or voltage against p/m percent. (Instrument may be calibrated to read directly in p/m or percent). Record the concentration of lead of the unknown sample and report it as percent of the lead in total paint. If the percent of the nonvolatile vehicle is known, divide percent lead obtained based on total paint (A) by the percent of the nonvolatile vehicle (B) to obtain the percent of lead based on nonvolatile vehicle (C) $\% C = \frac{A}{B} \times 100$.

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